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Mobility of Plutonium and Americium through a Shallow Aquifer in a Semiarid Region

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■ Treated liquid wastes containing traces of plutonium and americium are released into Mortandad Canyon, within the site of Los Alamos National Laboratory, NM. The wastes infiltrate a small aquifer within the canyon. Although laboratory studies have predicted that the movement of actinides in subsurface environments will be limited to less than a few meters, both plutonium and americium are detectable in monitoring wells as far as 3390 m downgradient from the discharge. Between the first and last monitoring wells (1.8 and 3.4 km from the discharge), plutonium concentrations decreased exponentially from 1400 to 0.55 mBq/L. Americium concentrations ranged between 94 and 1240 mBq/L, but did not appear to vary in a systematic way with distance. Investigation of the properties of the mobile actinides indicates that the plutonium and part of the americium are tightly or irreversibly associated with colloidal material between 25 and 450 nm in size. The colloiddally bound actinides are removed only gradually from the groundwater. The fraction of the americium not associated with colloids exists in a low molecular weight form (diameter, ≤ 2 nm) and appears to be a stable, anionic complex of unknown composition. The mobile forms of these actinides defeat the forces that normally act to retard their movement through groundwater systems.

Introduction

Treated waste effluents from the Central Waste Treatment Plant at the Los Alamos National Laboratory have been discharged into Mortandad Canyon since 1963. The canyon drains in an easterly direction from the Pajarito Plateau upon which the laboratory complex is located and has been the subject of extensive study (1-5). The shallow alluvium of Mortandad Canyon is composed of lensed sandy to silty clay materials formed by weathering of volcanic rocks (Bandelier Tuff) and contains a small elevated aquifer of $(20-30) \times 10^3$ m³ storage capacity (see Figure 1). Annual storm runoff into the canyon ranges from 25 to 125×10^3 m³ per year. Treated waste

effluents are released into the seasonal stream, flow down the canyon and, under ordinary conditions, infiltrate into the tuff within ~ 2 km (1). Surface water may flow as far as 3.4 km beyond the waste outfall during storm events. Subsurface flow represents $\sim 90\%$ of the water movement in the canyon. Tritium oxide tracer experiments have shown that 85% of the water released from the waste plant is lost through evapotranspiration. Total transit time for the tritium from the waste outfall to a monitoring well 3390 m down the canyon was about a year (2). The water that does not evaporate is assumed to be lost by infiltration into the underlying tuff, because no continuous surface flow exists along the reach of the canyon.

The waste treatment process includes the addition of iron sulfate and lime (6). The precipitation of iron hydroxides and calcium carbonate acts to remove almost all of the actinides from the waste, although traces of ²³⁸Pu, ^{239,240}Pu, and ²⁴¹Am remain in the effluent and are released to the canyon (7, 8).

The shallow aquifer contains a series of monitoring wells. Sampling of these wells has revealed that plutonium and americium are found in the groundwater at distances of 3400 m from the outfall (7, 8). Some of the actinides could be transported to the lower region of the canyon by surface flow during occasional storm events. However, the tritium oxide transit time measurements suggest that the majority of water movement takes place in the subsurface. Reports of plutonium and americium movement in groundwater over distances of even a few meters are rare (9, 10). It was the purpose of this study to determine the true mobility of these actinides in the groundwaters of Mortandad Canyon and to establish the features of either the wastewater or the aquifer that might contribute to enhanced mobility. These studies are part of the United States Department of Energy's Subsurface Science Program, which is developing a better fundamental understanding of contaminant transport in groundwater systems.

Regular monitoring of the effluents and groundwater has confirmed that all effluents are contained within the laboratory boundary, that the concentrations of plutonium and americium have not exceeded the Department of Energy Concentration Guidelines for Controlled Areas, and that no water is derived from Mortandad Canyon for drinking, industrial, or agricultural purposes (11, 12). These trace level actinides, however, act as excellent tracers

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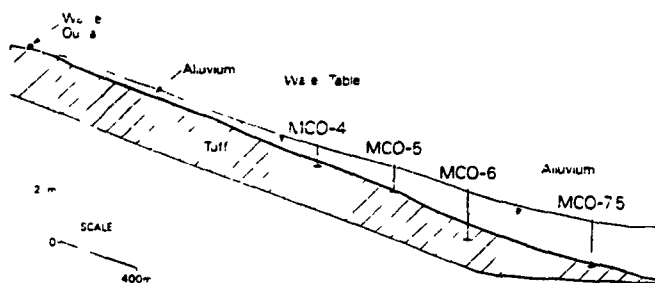


Figure 1 Cross-sectional schematic of Mortandad Canyon aquifer system showing the location of the monitoring wells

Table I Surface Sampling Station and Monitoring Wells in Mortandad Canyon (March 1983)^a

| parameter | surface | MCO-4 | MCO-5 | MCO-6 | MCO-7.5 |
|--------------------------|---------|-------|-------|-------|---------|
| distance from outfall, m | 1900 | 1807 | 2235 | 2660 | 3390 |
| depth of well, m | | 5.2 | 7.3 | 12.5 | 18.6 |
| depth to water, m | | 1.2 | 4.3 | 9.1 | 13.1 |
| pump depth, m | | 4.4 | 6.6 | 11.9 | 18.0 |
| sampling rate, L/min | | 4.1 | 2.8 | 3.8 | 1.9 |

^a Distances are measured along the stream bed

to evaluate the potential for colloidal transport of subsurface groundwater contaminants. These contaminants include actinides and other radionuclides, toxic metals, and toxic organic materials.

Experimental Section

Sampling Sampling took place in May and July 1982 and March 1983, from a series of monitoring wells originally installed by the U.S. Geological Survey. A cross-section diagram of the canyon and the location of the pertinent monitoring wells is shown in Figure 1. Hydrologic characteristics of the sampling stations are listed in Table I. Surface water was sampled from the stream at a location near the first well (MCO-4). An Isco well-sampling pump was used to draw water from the wells at 2–4 L/min. The wells were pumped continuously for 30 min, and then the sample was taken by pumping directly through a 29.3-cm-diameter, 0.45- μ m Millipore filter (type HAWP) into 25-L sample bottles, which were completely filled before capping. Measurements of temperature, oxygen, pH, and E_h were performed by pumping water directly through a series of in-line cells containing the sensors for a dissolved oxygen analyzer (Yellow Springs Instruments, Model 57) and a pH meter (Cole-Parmer Chem-Cadet) with a combination pH electrode and platinum electrode. Subsurface samples were made to 1 M concentration in HNO_3 and spiked with internal standards of ^{242}Pu in the reduced (IV) state (13) and ^{243}Am . For measurements of plutonium oxidation states, ^{238}Pu was also added in the oxidized (VI) valence state (13). The surface water samples, subsurface samples, and 0.45- μ m filters were shipped to Argonne National Laboratory for analysis.

Actinide Analysis The water samples were evaporated to a small volume over low heat and digested with nitric acid. The digest was analyzed for isotopes of plutonium and americium by established methods (14–16). The filters were ashed at 525 °C and the residual ash was weighed. The ash was then dissolved in hydrochloric acid and analyzed for the actinides. The distribution coefficients (K_d) were calculated as the ratio of the radioactivity per kilogram of ash to the radioactivity per liter of filtrate.

Contributions of dissolved salts to the ash weights were estimated to be less than 2%.

Oxidation-state distributions of plutonium were measured by the rare-earth fluoride fractionation of Nelson and Lovett (14). The plutonium in the samples was observed to be $\geq 90\%$ in the reduced, particle active state.

Sample Fractionation The size distribution of the actinides for a water sample from well MCO-5 was determined by sequential passage of a sample through filters of progressively smaller size. A 15-L sample of water was first filtered through a 0.45- μ m Millipore filter. Internal standards of ^{242}Pu and ^{243}Am were added to 10 L of the filtrate and 2 days was allowed for exchange with the ambient isotopes. The solution was then filtered through a 0.025- μ m (25-nm) Nuclepore polycarbonate filter. Ultrafiltration was carried out with a 100 000 molecular weight (MW) membrane (Amicon Corp., Danvers, MA) under nitrogen pressure in an Amicon Model 2000 apparatus, followed by a 10 000 MW Amicon membrane. The ultrafiltration was not allowed to go to completion because we observed that the concentrated colloidal materials would pass through the filter as the membrane became dry. Near the end of the filtration, the concentrate and the filter were recovered and analyzed separately, and the actinide measurements were combined. The nominal pore sizes of the ultrafiltration membranes were about 5 and 2 nm, respectively.

The filters and concentrates were analyzed as before. In some cases, subsamples of the filtrates were also analyzed as a cross check on the recovery of the actinides. Since the samples already contained ^{242}Pu and ^{243}Am , internal standards of ^{236}Pu and ^{244}Cm were used to maintain that actinide recovery was complete. Curium chemical recovery and chemical behavior has been accepted as being indistinguishable from americium.

Ion-Exchange Properties The samples taken for these experiments were pumped from the wells directly through 0.45- μ m filters for 10 min into 1-L bottles containing an ion-exchange resin. The liquid was decanted and the resin washed twice with distilled water. The sample and rinse water were combined and evaporated to dryness. The resin was ashed in a muffle furnace and was analyzed for both plutonium and americium. Cationic species were determined with cation-exchange resin (H form, 27 g/L). Anionic forms were similarly detected with anion-exchange resin (Cl form, 27 g/L). Neutral species were determined by contacting samples with mixed cation and anion resins (H and Cl forms, 27 g/L of each) and analyzing the supernatant liquid.

Other Analyses The particulate material was examined using energy-dispersive X-ray fluorescence by the Analytical Chemistry Group of the Chemistry and Laser Science Division of Los Alamos National Laboratory (LANL). Mineralogy of the particulate material was examined using X-ray diffraction, carried out by the Physical Metallurgy Group of the Materials Sciences and Technology Division of LANL. Analyses of ferrous iron and total iron were done by reaction with 1,10-phenanthroline (17). Dissolved silica was determined by the molybdosilicate method (18). Other analytical water chemistry was carried out by the Environmental Science Group at LANL, according to standard methods (19). Waste discharge data were provided by the Waste Management Group of LANL.

Results and Discussion

Water Chemistry Filtered water samples taken from the surface sampling location and from the four monitoring wells were analyzed for conventional water chemistry parameters (Table II). The most noticeable variations in

Table II Chemical and Physical Characteristics of the Waters Sampled in March 1983^a

| parameter | surface | MCO-4 | MCO 5 | MCO-6 | MCO-7 5 |
|-------------------------------------|---------|-------|-------|-------|---------|
| temp, °C | | 28 | 66 | 72 | 80 |
| oxygen | 65 | 07 | 07 | 03 | 43 |
| pH | 10.1 | 10.0 | 7.0 | 6.9 | 6.4 |
| H _b , mV | 275 | 205 | 266 | 245 | 303 |
| conductivity, dS/m | 12 | 12 | 13 | 13 | 14 |
| ammonia | 06 | 03 | 00 | 00 | 00 |
| fluoride | 39 | 62 | 55 | 42 | 05 |
| sulfate | 137 | 150 | 162 | 161 | 260 |
| alkalinity (as CaCO ₃) | 211 | 196 | 167 | 191 | 184 |
| carbonate (as CaCO ₃) | 141 | 105 | 66 | 59 | 00 |
| bicarbonate (as CaCO ₃) | 63 | 87 | 160 | 185 | 184 |
| DOC | 20 | 20 | 21 | 22 | 4 |
| nitrate | 340 | 360 | 430 | 400 | 450 |
| nitrite | 43 | 45 | 46 | 04 | 01 |
| total phosphate (as P) | 85 | 19.0 | 7.4 | 2.6 | 0.8 |
| orthophosphate (as P) | 63 | 14.3 | 5.3 | 2.3 | 0.5 |
| hydrolyzable P | 00 | 00 | 00 | 01 | 03 |
| organic P | 24 | 48 | 21 | 02 | 00 |
| sulfide ^b | nd | nd | nd | nd | nd |
| silica | 32 | 25 | 21 | 26 | 30 |
| total iron | 23 | 27 | 38 | 20 | 01 |
| ferrous iron (% of total iron) | 57.8 | 47.4 | 27.6 | 41.1 | 31.1 |
| aluminum | 48 | 49 | 70 | 38 | 00 |
| calcium | 16.2 | 8.0 | 15.9 | 19.3 | 60 |
| magnesium | 06 | 06 | 39 | 49 | 15.5 |
| potassium | 20.4 | 11.5 | 5.4 | 5.5 | 7.8 |

^a All units are in mg/L unless otherwise stated ^b Sulfide was below limits of detection of 0.004 mg/L

Table III Mineral Phases Predicted To Be Supersaturated in the Surface and Well Water Samples by Using WATEQ^a

| mineral phase | surface | MCO-4 | MCO-5 | MCO-6 | MCO-7 5 |
|--|---------|-------|-------|-------|---------|
| Phases That Remain Supersaturated | | | | | |
| fluorapatite | xx | xx | xx | xx | xx |
| iron oxyhydroxides (e.g., goethite, gibbsite, hematite) | xx | xx | xx | xx | xx |
| Phases That Become Unsaturated with Distance | | | | | |
| calcium carbonate (calcite, aragonite) | x | x | o | o | o |
| aluminas (boehmite, diaspore) | x | x | xx | x | o |
| chlorite, prehnite | xx | xx | o | o | o |
| hydroxyapatite | xx | xx | o | o | o |
| aluminosilicates (clays, micas, zeolites) | xx | xx | xx | xx | o |
| silicates (talc, tremolite) | xx | xx | o | o | o |
| Phases That Are Transient or Become Supersaturated with Distance | | | | | |
| α-alumina | o | o | x | x | o |
| aluminosilicates | o | o | xx | xx | o |
| dolomite | o | x | o | o | o |
| iron phosphates (strengite, vivianite) | o | o | x | x | x |

^a Phases with a positive computed saturation index (CSI) are listed. The codes used in the table are as follows: x, for a CSI ranging from 0 to 3 (slightly supersaturated), xx, for CSI greater than 3 (very supersaturated), and o for negative values (unsaturated).

the water chemistry with distance from the waste outfall were (a) the decreases in phosphate, iron, nitrite, and potassium, (b) the increases in calcium and magnesium, and (c) the decline in pH from the high value in the wastewater to near-neutrality. The alkaline nature of the wastewater could have favored leaching of elements such as silicon and aluminum from the aquifer matrix. As the pH declined with distance, these elements could reprecipitate on immobile surfaces or persist as colloidal materials.

The low oxygen concentrations in the monitoring wells MCO-4, MCO-5, and MCO-6 indicated a situation of potential importance. Under anoxic conditions, we could have expected ferrous iron to be leached from the aquifer matrix. It would have reprecipitated upon encountering oxygen, producing colloidal materials and particulates. In addition, we observed that the measured concentrations of calcium and orthophosphate in surface waters and the MCO-4 well were supersaturated.

To further evaluate these observations, we used the available data in Table II to calculate the predicted

equilibrium concentrations using the WATEQ model (20). Table III lists the mineral phases as identified by WATEQ that could be expected to be supersaturated in the samples. Although the equilibrium model results can only be considered as rough estimates, they do indicate that colloidal materials containing iron oxides, clays, and hydroxy- and fluorapatites may exist in the subsurface waters and persist as far as the MCO-7 5 well.

Particulate material caught on a 0.45-μm filter was subjected to mineralogical analysis by X-ray fluorescence and X-ray diffraction. X-ray fluorescence analysis confirmed that both calcium and iron were present in the particulate material. The presence of both of these elements in the solid phase was predicted by the WATEQ analysis of the water chemistry data. X-ray diffraction analysis also confirmed that siliceous minerals were present.

Mobility of Actinides The concentrations of ^{239,240}Pu and ²⁴¹Am in water from four selected sampling wells are shown in Figure 2 for May 1982 and March 1983. The

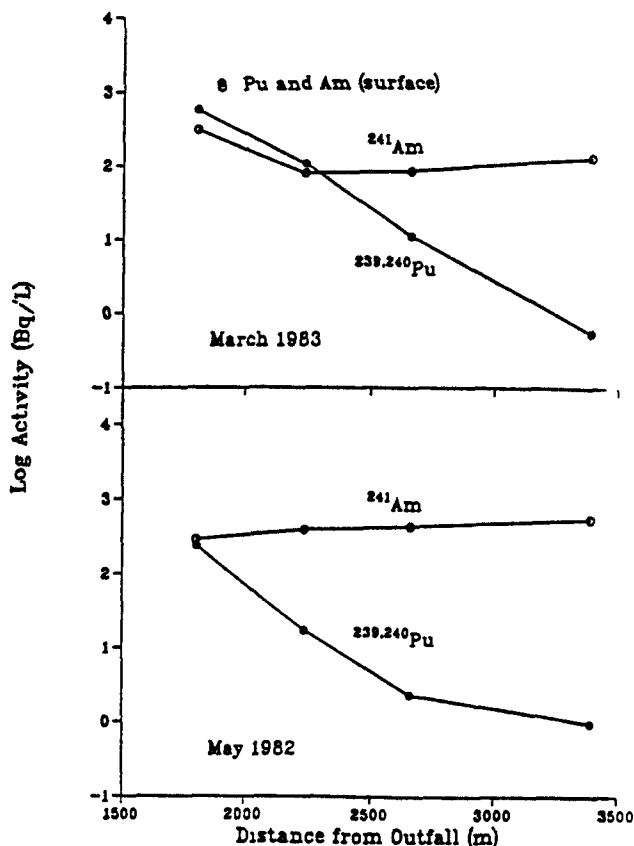


Figure 2 Concentrations of plutonium and americium in wells MCO-4, MCO-5, MCO-6, and MCO-7 5 in May 1982 and March 1983. The ordinate is distance in meters from the waste outfall.

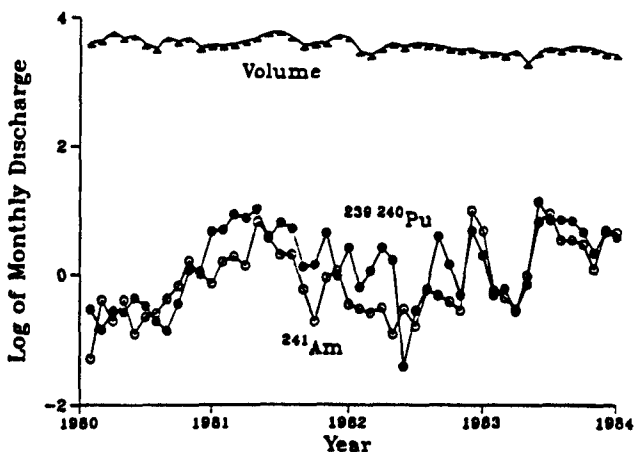


Figure 3 Total curies of plutonium and americium and total volumes (10^3 L) of monthly discharges to Mortandad Canyon from January 1980 to April 1983.

concentrations of americium remained relatively constant between the nearest and farthest wells. The plutonium concentration decreased in a nearly exponential fashion with distance. We considered that the variations in the discharge rates of the two elements might explain the different behavior. Discharge data for the years 1980 to 1983 are shown in Figure 3. There were dramatic variations in the relative discharge rates of plutonium and americium. Plutonium concentrations varied as much as 100-fold around the time of the sampling in 1982-1983. The time scale of the fluctuations in the discharges was on the order of weeks, whereas the travel time over the length of the aquifer would be at least a year. We concluded that the systematic decline of the plutonium con-

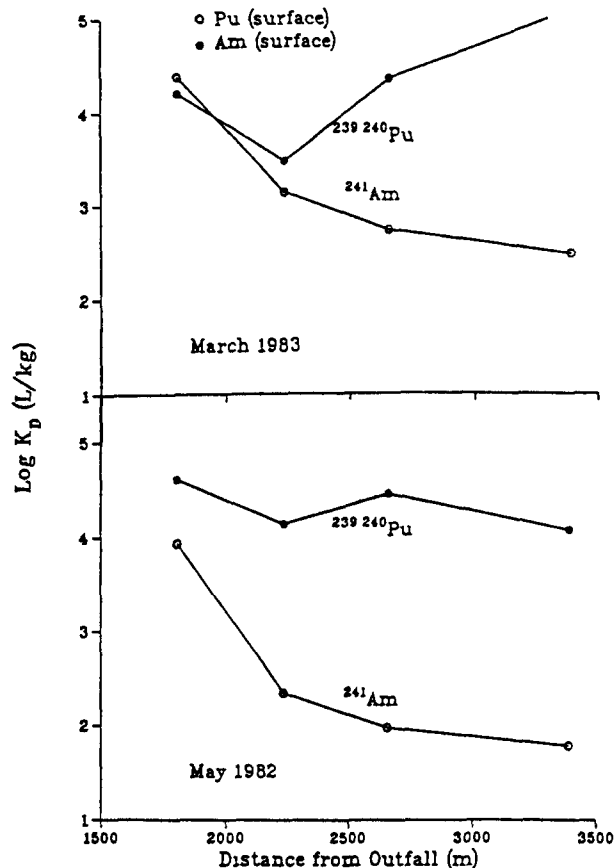


Figure 4 Distribution coefficients for actinides in the aquifer in May 1982 and March 1983.

centrations and the different behavior of the two actinides with distance was a consequence of movement through the aquifer and not caused by fluctuations in the discharge.

This conclusion was further supported by isotope ratio data obtained from the Environmental Surveillance Group of LANL (7, 8, 11, 12, 21-25). In 1978, the amount of discharged ^{239}Pu and ^{240}Pu increased dramatically relative to the amount of ^{238}Pu . We calculated the ratio of $^{239,240}\text{Pu}$ to ^{238}Pu from available data for each well and the advancing front of $^{239,240}\text{Pu}$ could be followed. Between wells MCO-4 and MCO-6, a distance of 860 m, the travel time was ~ 2 years. Thus, the rate of movement of the plutonium was $\sim 1/2$ km per year. We therefore expect that the week-to-week fluctuations of actinide discharges, although appreciable, will be dampened by the much slower movement in the subsurface.

The distribution coefficients (K_D values) of the plutonium and americium onto particles ($\geq 45 \mu\text{m}$) are displayed in Figure 4. The apparent K_D values for plutonium were relatively constant or increasing over the distance between MCO-4 and MCO-7 5. The plutonium was $\sim 90\%$ in the reduced state for these experiments. However, the apparent adsorption behavior of americium to $\geq 45\text{-}\mu\text{m}$ particles decreased systematically with distance. In the last well, it was barely adsorbed at all. Such behavior is unexpected for an element that is generally considered to be strongly adsorbed to particles.

The K_D for plutonium is lower by about an order of magnitude than that observed in many other water bodies (15). In surface waters, the K_D has been seen to be inversely related to the dissolved organic carbon (DOC) concentration (15, 26). Since the DOC concentrations in the Mortandad Canyon groundwater were found to be elevated (see Table II), it was proposed that this same

Table IV Distribution Coefficients (K_D Values) for ^{242}Pu onto Sediment from Mortandad Canyon and from Lake Michigan

| water source | sediment source | K_D , L/kg $\times 10^{-4}$ |
|---------------|-----------------|-------------------------------|
| Mortandad | Mortandad | 2 |
| Mortandad | Lake Michigan | 10 |
| Lake Michigan | Mortandad | 9 |
| Lake Michigan | Lake Michigan | 200 |

Table V Concentrations of $^{239,240}\text{Pu}$ and ^{241}Am in Size Fractions of Well Water from MCO-5, March 1983^a

| size class retained, nm | plutonium | | americium | |
|-------------------------|-------------|-------|-------------|-------|
| | concn | ratio | concn | ratio |
| >450 | 31.8 (0.9) | | 21.7 (1.0) | |
| 25-450 | 141.3 (6.4) | 0.18 | 72.9 (3.3) | 0.99 |
| 5-25 | 0.8 (0.1) | 6.94 | 2.0 (0.1) | 2.74 |
| 2-5 | 11.3 (0.3) | 6.21 | 68.9 (2.2) | 0.78 |
| <2 (filtrate) | 8.4 (0.6) | 6.94 | 113.3 (5.0) | 0.37 |
| <450 (total) | 165.9 (6.4) | 1.18 | 264.8 (9.5) | 0.71 |

^a Filter sizes and corresponding size fractions are as follows: 0.45 μm (>450 nm), 0.025 μm (25-450 nm), 100 000 MW ultrafilter (5-25 nm), and 10 000 MW ultrafilter (2-5 nm). Standard counting errors are given in parentheses. Also shown is the ratio of added isotope to ambient isotope for the two elements. Concentrations are in mBq/L.

correlation may exist in subsurface waters. K_D values of added ^{242}Pu were measured in sediment and water recovered from Mortandad Canyon and compared with water and sediment from Lake Michigan. Lake Michigan materials were chosen because they have been used as reference materials in past work (26) and are low in DOC (1.4 mg/L). The results of this experiment are shown in Table IV. The K_D values of plutonium onto sediment from either source were notably greater when measured in Lake Michigan water than in Mortandad Canyon water. This suggests that the water chemistry is at least partially responsible for the lower K_D values.

Characterization of the Ambient Actinides Since the absolute amounts of the actinides in the groundwaters were very small, they were characterized both physically and chemically by using tracer methods. A sample of water from MCO-5 was spiked with ^{242}Pu and ^{243}Am and left to stand for 2 days to allow the added actinides to equilibrate with the isotopes originally present. They were then size-fractionated, as described previously, by ultrafiltration techniques. The concentrations of added and ambient isotopes were then determined for each size fraction.

A white material remained insoluble in the filtrate from every size-fractionated sample and, since it was insoluble in nitric or hydrochloric acid, was thought to be silica. Results are given in Table V. Of the ambient plutonium, 85% was found to be retained by the 25-nm filter, corresponding to colloidal materials between 25 and 450 nm in size. The ambient americium was distributed somewhat differently than the plutonium. While 28% of the americium was found in the 25-450-nm size class, 26% was associated with colloidal materials of 2-5 nm size. The largest fraction, ~43%, was small enough to pass through every filter.

An important feature of this experiment was the behavior of the added isotopes, ^{242}Pu and ^{243}Am , relative to the ambient ones. If the ambient actinides were readily available to participate in sorption-desorption reactions, they would exchange with their added equivalents. The ratios of added to ambient isotopes would therefore be the same in every fraction. The difference in the ratio between

Table VI Relative Distribution (%) of Charged Actinide Species^a

| water source | anionic | cationic | neutral |
|---------------|---------|----------|---------|
| Plutonium | | | |
| waste outfall | 7 | <2 | 94 |
| surface | 3 | <2 | 93 |
| MCO-4 | 2 | <2 | 99 |
| MCO-5 | 3 | <2 | 96 |
| MCO-6 | 4 | <2 | 91 |
| MCO-7.5 | 8 | <2 | 94 |
| Americium | | | |
| waste outfall | 11 | 11 | 78 |
| surface | 3 | <2 | 97 |
| MCO-4 | 3 | <2 | 98 |
| MCO-5 | 17 | <2 | 84 |
| MCO-6 | 46 | <2 | 63 |
| MCO-7.5 | 31 | <2 | 93 |

^a The radioactivities retained by anion and cation resins, and those not retained by the mixed resins, are expressed as percentages of the total actinide concentration.

the retained and filtered fractions is an inverse measure of the degree of exchange that occurs between the added and ambient isotope over the 2-day equilibration period.

The expected equilibration of plutonium isotopes among the size classes did not occur. Filtration through the 25-nm Nucleopore filter caused a dramatic decrease in the ratio of added to ambient isotope. The ambient $^{239,240}\text{Pu}$ was preferentially retained by this filter, relative to the added ^{242}Pu . Therefore ambient plutonium, located in the 25-450-nm size fraction, was bound by colloidal materials in such a way that exchange was not taking place during the time frame of the experiment. The remaining ambient plutonium (approximately 15%) was distributed over the other size classes and was found to be equally exchangeable in each fraction.

The behavior of americium was quite different. The material on the 100 000 MW filter had a higher ratio of added to ambient isotopes than the initial solution. Added americium was therefore retained most effectively in this size range, and this indicates that adsorption sites are still available for binding americium. The other fractions are all reasonably close to the added to ambient ratio expected if the americium is exchanging, with the possible exception of the less than 2-nm fraction. In this fraction the americium is less available for exchange, which would be consistent with the observation of this fraction being quite mobile in the aquifer system, at least as far as well MCO-5.

The 10 000 MW filter, on the other hand, retains material with a decreased ratio, and in the final filtrate, the ratio is lower still. These results may be explained by assuming the ambient americium is bound irreversibly to colloidal materials smaller than 100 000 MW. Added americium would be free to bind to the larger colloidal materials similar to the ambient and would be fractionated similarly.

Results of ion-exchange experiments are shown in Table VI. In natural waters, plutonium(IV) is normally in the anionic form due to complexation with carbonate and humic substances, while americium normally is in cationic forms (15). In Mortandad Canyon surface water and groundwater, plutonium behaved primarily as a neutral species. Americium, on the other hand, exhibited a combination of anionic and neutral behavior in all of the samples that had been in contact with the alluvium. The proportion of anionic americium increased with distance from the source. Cationic americium was only found in the waste outfall, before it has contacted stream sediments or the aquifer matrix. The proportion of anionic ameri-

cium varied from a negligible fraction in the surface sample and MCO-4 to nearly half of the total in the lower wells

Conclusions

It is true that the aquifer matrix in Mortandad Canyon is not a particularly effective adsorbent for plutonium. Nevertheless, in the groundwater environments, an apparent K_D of 20 000 is still large enough to retard the movement of plutonium over a short distance. Other workers, studying the volcanic tuff in the Los Alamos area (27-29) have demonstrated that plutonium and americium do in fact move further through the tuff than through other soils or sediments, but these movements are never more than a few tens of meters. Isotope-exchange experiments demonstrated that the plutonium bound to the colloidal materials of 25-450-nm size is not exchangeable. It is therefore unavailable to exchange among adsorption sites on the immobilized solids in the aquifer and would not be subject to the normally estimated retarding forces.

About half of the americium seemed to be located in a nonexchanging anionic species of a small size (≤ 2 nm). The adsorption (K_D of ambient americium onto large particles $\geq 0.45 \mu\text{m}$) was seen to decrease with distance down the canyon. This may be due to gradual filtration of americium associated with the larger colloids, leaving only the low molecular weight material in the groundwater. Large fractions of both americium and plutonium were observed to travel in the aquifer over similar distances. This further implies that the high molecular weight fraction of the americium (about half) must have been associated irreversibly with mobile colloids in the same way as the plutonium. It is also likely that the americium associated with large colloids would be removed from the groundwater at about the same rates as plutonium. The reason that the total americium does not become depleted with distance (Figure 2) is because nearly half of it is associated with less than 2-nm material, which is not as rapidly removed as the larger colloidal materials. As well, evaporation of water from the shallow elevated aquifer (2, 3) would act to concentrate this remaining low molecular weight americium complex.

We feel that there is very strong evidence that the actinides, plutonium and americium, are associated with colloidal materials in a way that is effectively irreversible. Even very slow adsorption-desorption reactions, with time constants of months, would allow the actinides to be adsorbed to the aquifer matrix over relatively short distances.

The observation that the apparent K_D value of americium decreases dramatically with distance helps to resolve the question of surface transport of actinides down the canyon. If storm events had transported the actinides down the reach of the canyon by surface flow, we would have expected all species of americium less than a few microns in size to be transported in the surface flow with about equal efficiency. The apparent K_D of americium (i.e., the relative amounts of americium in the ≥ 0.45 - and ≤ 0.45 - μm fractions of the groundwater would have been similar in each sampling well, although the concentration might vary. The systematic change in the K_D s for americium as a function of distance in the aquifer suggests that it is transported predominantly by subsurface flow at least as far as well MCO-7.5.

Some of the americium was undoubtedly discharged in the same form as the plutonium and was borne by the colloidal material, but the remainder was of very low molecular weight, and its chemical nature is unknown. It is possible that a stable complex of americium was produced by operations within the Los Alamos Laboratory site, or as a result of the waste treatment process, and

discharged from the Laboratory as a low molecular weight complex whose particle reactivity was very slight and whose exchange rate was so slow that it could persist for years under the conditions in the aquifer. It is also possible that the americium could be interacting with natural complexing agents in the aquifer.

These observations have suggested that colloidal materials can be mobile in groundwater systems for great distances and are capable of binding and transporting radionuclide contaminants in subsurface systems. Similar observations of colloid-mediated mobility of radionuclides in groundwater have recently been made (30-32). It is likely that colloid-mediated mobility of radionuclides and other contaminants will be encountered in many other locations once investigators have become aware of its importance. Clearly, as pointed out in a recent feature article (33), colloidal materials may be important means of mobilizing not only actinides, but toxic metals and organics as well. Further information regarding both natural and waste-derived colloidal materials and their physical and chemical properties will be necessary if we are to accurately predict the mobility of groundwater pollutants.

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Kinetic Approach to Trace Metal Complexation in Seawater: Application to Zinc and Cadmium

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■ Anodic stripping voltammetry (ASV) using a rotating disk electrode, along with ion-exchange procedures in the column and batch modes were used to study the lability characteristics of zinc and cadmium in Narragansett Bay seawater. By combining the three techniques into one single scheme, the effective time of measurement can be varied in a controlled way between 10^{-2} and 10^6 s. Application of this procedure to zinc and cadmium showed that the labile fraction of the metal was a function of measurement time over the entire range. The species of a metal in natural waters can be characterized directly on the basis of lability dependence with time.

Introduction

It is now well established that the total metal concentration in a water sample is rarely adequate to assess the reactivity of that metal in biological or geochemical processes (3, 12). Some characterization of the physicochemical forms of the metal, together with the rates of transformation among these forms, is a prerequisite for understanding global processes. For example, being able to explain the observed distribution of a metal in the sea through fundamental physicochemical principles would open the door to the prediction of future distributions, e.g., given a change in anthropogenic inputs. The investigation of chemical speciation requires measurements of an untreated sample. The composition of the sample with respect to the major elements, pH, organic ligands, redox state, and adsorption sites must be kept as constant as possible, since chemical speciation is dictated by these parameters. In the absence of adequate techniques, pro-

cedures have been used that involve reanalyzing the sample after applying successively harsher chemical steps such as lowering of pH. As the results from these speciation procedures are operationally defined, Davison (1) recommended that the effective time of measurement be reported in all electroanalytical work so that measurements performed by different workers under different experimental conditions could be compared.

The speciation method of Figura and Mc Duffie (2) subdivides the dissolved metal into categories described as labile, moderately labile, slowly labile, and inert, based upon the concentrations measured by anodic stripping voltammetry (ASV) at pH 6.3 and Ca-Chelex ion exchange in successive column and batch procedures. The terminology they used implies a simple kinetic basis for the discrimination between "detectable" vs "undetectable" metal. This approach is based on the premise that the magnitude of each fraction may be controlled by some slowly dissociating species not (or partially) detected by the corresponding technique, and it ignores the possibility of species shifts upon buffering to pH 6.3. These fractions are defined at some arbitrary measurement times and may therefore be only loosely related to the unknown species. This fractionation of total dissolved metal into four identifiable categories is based on operationally defined procedures rather than actual chemical or physical properties.

In this paper we use three techniques to characterize the time scales of exchange for the species comprising the total metal concentration of Zn and Cd in marine systems. With increasing cumulated time, one observes the contributions of progressively more inert species. This scheme distin-